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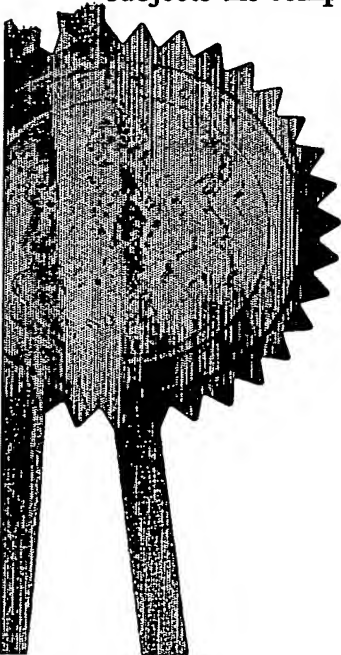
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06JUN03 E812842-4 C03022
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Request for grant of a patent

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1. Your reference	10018		
2. Patent application number (The Patent Office will fill in this part)	0312970.7		5 JUN 2003
3. Full name, address and postcode of the or of each applicant (underline all surnames)	BP CHEMICALS LIMITED BRITANNIC HOUSE 1 FINSBURY CIRCUS LONDON EC2M 7BA UNITED KINGDOM Patents ADP number (if you know it) If the applicant is a corporate body, give the country/state of its incorporation		
	4141891002		
4. Title of the invention	PROCESS FOR THE PRODUCTION OF OLEFINS		
5. Name of your agent (if you have one)	PREECE, Michael PATENTS & AGREEMENTS BP INTERNATIONAL LIMITED CHERTSEY ROAD SUNBURY-ON-THAMES MIDDLESEX, TW16 7LN UNITED KINGDOM		
"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)	4030177002		
Patents ADP number (if you know it)			
6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number	Country	Priority application number (if you know it)	Date of filing (day / month / year)
7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)	
8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if: a) any applicant named in part 3 is not an inventor, or b) there is an inventor who is not named as an applicant, or c) any named applicant is a corporate body. See note (d))	YES		

Patents Form 1/77

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Continuation sheets of this form

Description 6

Claim(s) -

Abstract -

Drawing(s) -

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature *M. Ke*
PREECE, Michael

Date 5th June 2003

12. Name and daytime telephone number of person to contact in the United Kingdom

(01932) 763201

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PROCESS FOR THE PRODUCTION OF OLEFINS

The present invention relates to a process for the production of olefins from hydrocarbons in which the hydrocarbons are treated to autothermal cracking.

Autothermal cracking is a new route to olefins in which the hydrocarbon feed is mixed with oxygen and passed over an autothermal cracking catalyst. The autothermal cracking catalyst is capable of supporting combustion beyond the fuel rich limit of flammability. Combustion is initiated on the catalyst surface and the heat required to raise the reactants to the process temperature and to carry out the endothermic cracking process is generated in situ. Generally the hydrocarbon feed and the oxygen is passed over a single catalyst bed to produce the olefin product. Typically, the catalyst bed comprises at least one platinum group metal, for example, platinum, supported on a catalyst support. The autothermal cracking process is described in EP 332289B; EP-529793B; EP-A-0709446 and WO 00/14035.

The catalyst supports are usually ceramic materials and are usually in the form of foam, pellets, beads, spheres, tablets and/or extrudates. However these can often be thermally unstable which results in support cracking. In addition these supports are usually structured to provide tortuous flow regimes for the gaseous reactants. Whilst these materials provide good mixing of the reactants and promote reaction stability they can create a high pressure drop in the autothermal reactor which leads to excessive force being applied to the catalyst which can lead to structural collapse.

Consequently there is a need to provide supports that are thermally stable and also provide a low pressure drop in the autothermal reactor.

Accordingly, the present invention provides a process for the production of an

olefin, said process comprising passing a mixture of a hydrocarbon and an oxygen-containing gas over a catalyst capable of supporting combustion beyond the fuel rich limit of flammability to produce said olefin wherein the catalyst comprises a catalytic component and a metallic structured packing and wherein the structured packing
5 comprises a multiplicity of open ended channels.

Preferably, the catalyst component comprises a Group VIII B metal. Suitable Group VIII B metals include platinum, palladium, ruthenium, rhodium, osmium and iridium. Preferably, the Group VIII B metal is selected from rhodium, platinum, palladium or mixtures thereof. Especially preferred are platinum, palladium or mixtures
10 thereof. Typical Group VIII B metal loadings range from 0.01 to 50 wt %, preferably, from 0.01 to 20 wt %, and more preferably, from 0.01 to 10 wt %, for example 1-5 wt%, such as 3-5 wt%. Suitably, the first catalyst bed comprises platinum or palladium, especially platinum.

Preferably the catalyst component may be a promoted catalyst component such
15 as a promoted Group VIII B metal catalyst. The promoter may be selected from the elements of Groups III A, IV A and V A of the Periodic Table and mixtures thereof. Alternatively, the promoter may be a transition metal; the transition metal being a different metal to the catalyst component, such as the Group VIII B metal(s) employed as the catalytic component.

20 The promoter may also be selected from any of the lanthanide metal oxides.

Preferred Group III A metals include Al, Ga, In and Tl. Of these, Ga and In are preferred. Preferred Group IV A metals include Ge, Sn and Pb. Of these, Ge and Sn are preferred, especially Sn. The preferred Group V A metal is Sb. The atomic ratio of Group VIII B metal to the Group III A, IV A or V A metal may be 1 : 0.1 - 50.0,
25 preferably, 1: 0.1 - 12.0, such as 1 : 0.3 - 5.

Suitable transition metal promoters may be selected from any one or more of Groups IB to VIII B of the Periodic Table. In particular, transition metals selected from Groups IB, IIB, VIB, VII B and VIII B of the Periodic Table are preferred. Examples of such transition metal promoters include V, Ni, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pt, Cu, Ag, Au, Zn, Cd and Hg. Preferred transition metal promoters are Mo, Rh, Ru, Ir, Pt, Cu and Zn, especially Cu. The atomic ratio of the Group VIII B metal to the transition metal promoter may be 1: 0.1 - 50.0, preferably, 1:0.1 - 12.0.
30

Specific examples of promoted Group VIII B metals for use as the promoted catalyst component include Pt/Ga, Pt/In, Pt/Sn, Pt/Ge, Pt/Cu, Pd/Sn, Pd/Ge, Pd/Cu and Rh/Sn. Where the Group VIII B metal is Rh, Pt or Pd, the Rh, Pt or Pd may comprise between 0.01 and 5.0 wt %, preferably, between 0.01 and 3.0 wt %, and more

5 preferably, between 0.5 and 3.0 wt % of the total weight of the catalyst. The atomic ratio of Rh, Pt or Pd to the Group IIIA, IVA, VA or transition metal promoter may be 1 : 0.1 - 50.0, preferably, 1: 0.1 - 12.0. For example, atomic ratios of Rh, Pt or Pd to Sn may be 1: 0.1 to 50, preferably, 1: 0.1 - 12.0, more preferably, 1: 0.2 - 5.0 and most preferably, 1: 0.3 - 5.0. Atomic ratios of Pt or Pd to Ge may be 1: 0.1 to 50, preferably,
10 1: 0.1 - 12.0, and more preferably, 1: 0.5 - 8.0. Atomic ratios of Pt or Pd to Cu may be 1: 0.1 - 3.0, preferably, 1: 0.2 - 2.0, and more preferably, 1: 0.3 - 0.5.

For the avoidance of doubt, the catalyst component and the promoter may be present in any form, for example, as a metal, or in the form of a metal compound, such as an oxide.

15 The metallic structured packing may be selected from any suitable metal. Suitable metals may include steel (mild and high carbon), stainless steel, hastaloy, Ni-Chrome, Inconel, Monel, nickel, copper, iron, platinum, noble metals and their alloys, cobalt, FeCrAlY, or any alloy containing Y, Cr, Fe, Ni and Al e.g Kanthal, Incoloy MA956 or CoCrAlY.

20 The metallic structured packing may be in the form of a foam but is preferably in the form of a channeled monolith. The structural dimensions of the metallic structured packing may vary.

Wherein the metallic structured packing is in the form of a foam, the foams usually have a pore size in the range of 10pores per inch (ppi) to 100ppi and preferably
25 between 30 to 45ppi. These foams typically have a density of from between 60% to 99% of theoretical density of a fully dense material.

Wherein the metallic structured packing is in the form of a monolith the monolith is usually provided with regular channels. These channels may be of any suitable shape the preferred ones being square, rectangular, triangular, hexagonal and
30 circular. Preferably the monolith is a honeycomb monolith. Typically the channels do not pass directly through the monolith and usually the channels provide a complex passageway through the monolith. Usually the monolith has between 2000cpi (cells per

inch) to 5cpi and preferably between 1000cpi to 10cpi.

The catalyst employed in the present invention may be prepared by any method known in the art. For example, gel methods and wet-impregnation techniques may be employed. Typically, the metallic structure packing is impregnated with one or more solutions comprising the catalyst component, dried and then calcined in air.

Prior to the addition of the catalyst component to the metallic structured packing the metallic structured packing may be at least partially coated with a non metallic coating. The non-metallic coating may be loaded onto the metallic structured packing by any method known in the art.

Suitable non metallic coatings are usually ceramic materials. Suitable ceramics include alumina, silica-alumina, a combination of alumina and mullite, lithium aluminium silicate, cordierite, silicon carbide, zirconia toughened alumina, partially stabilized zirconia, fully stabilized zirconia, spinel, chromia, titania, aluminium titanate, or any combination of the above.

The process of the present invention may be used to convert both liquid and gaseous hydrocarbons into olefins. Suitable liquid hydrocarbons include naphtha, gas oils, vacuum gas oils and mixtures thereof. Preferably, however, gaseous hydrocarbons such as methane, ethane, propane, butane and mixtures thereof are employed. Suitably, the hydrocarbon is a paraffin-containing feed comprising hydrocarbons having at least two carbon atoms.

The hydrocarbon feed is mixed with any suitable oxygen-containing gas. Suitably, the oxygen-containing gas is molecular oxygen, air, and/or mixtures thereof. The oxygen-containing gas may be mixed with an inert gas such as nitrogen or argon.

Additional feed components may be included, if so desired. Suitably, hydrogen, carbon monoxide, carbon dioxide or steam may be co-fed into the reactant stream.

Any molar ratio of hydrocarbon to oxygen-containing gas is suitable provided the desired olefin is produced in the process of the present invention. The preferred stoichiometric ratio of hydrocarbon to oxygen-containing gas is 5 to 16, preferably, 5 to 13.5 times, preferably, 6 to 10 times the stoichiometric ratio of hydrocarbon to oxygen-containing gas required for complete combustion of the hydrocarbon to carbon dioxide and water.

The hydrocarbon is passed over the catalyst at a gas hourly space velocity of

greater than $10,000 \text{ h}^{-1}$, preferably above $20,000 \text{ h}^{-1}$ and most preferably, greater than $100,000 \text{ h}^{-1}$. It will be understood, however, that the optimum gas hourly space velocity will depend upon the pressure and nature of the feed composition.

5 Preferably, hydrogen is co-fed with the hydrocarbon and oxygen-containing gas into the reaction zone. The molar ratio of hydrogen to oxygen-containing gas can vary over any operable range provided that the desired olefin product is produced. Suitably, the molar ratio of hydrogen to oxygen-containing gas is in the range 0.2 to 4, preferably, in the range 1 to 3.

10 Hydrogen co-feeds are advantageous because, in the presence of the catalyst, the hydrogen combusts preferentially relative to the hydrocarbon, thereby increasing the olefin selectivity of the overall process.

15 Preferably, the reactant mixture of hydrocarbon and oxygen-containing gas (and optionally hydrogen co-feed) is preheated prior to contact with the catalyst. Generally, the reactant mixture is preheated to temperatures below the autoignition temperature of the reactant mixture.

Advantageously, a heat exchanger may be employed to preheat the reactant mixture prior to contact with the catalyst. The use of a heat exchanger may allow the reactant mixture to be heated to high preheat temperatures such as temperatures at or above the autoignition temperature of the reactant mixture. The use of high pre-heat
20 temperatures is beneficial in that less oxygen reactant is required which leads to economic savings. Additionally, the use of high preheat temperatures can result in improved selectivity to olefin product. It has also be found that the use of high preheat temperatures enhances the stability of the reaction within the catalyst thereby leading to higher sustainable superficial feed velocities.

25 The process of the present invention may suitably be carried out at a catalyst exit temperature in the range 600°C to 1200°C , preferably, in the range 850°C to 1050°C and, most preferably, in the range 900°C to 1000°C .

30 The process of the present invention is usually operated at a pressure of greater than 0.5barg. Preferably the autothermal cracking process is operated at a pressure of between 0.5-40barg and advantageously between 10-30barg e.g. 15-25barg.

The reaction products are preferably quenched as they emerge from the reaction chamber to avoid further reactions taking place. Usually the product stream is cooled to

between 750-600°C within less than 100 milliseconds of formation, preferably within 50 milliseconds of formation and most preferably within 20 milliseconds of formation e.g. within 10 milliseconds of formation.

Wherein the autothermal cracking process is operated at a pressure of 5-20 barg
~~5 usually the products are quenched and the temperature cooled to between 750-600°C~~
within 20 milliseconds of formation. Advantageously wherein the autothermal cracking process is operated at a pressure of greater than 20 barg the products are quenched and the temperature cooled to between 750-600°C within 10 milliseconds of formation.

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The reaction products are preferably quenched as they emerge from the reaction chamber to avoid further reactions taking place. Usually the product stream is cooled to

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